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THE COORDINATION REACTIONS OF SILVER WITH SPECIAL REFERENCE TO THE ALKYNES

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Project Supervisor: Howard J. Lucas

Participants in Work: Alan E. Comyns
Forrest L. Carter and Thomas H. Applewhite

California Institute of Technology

Pasadena 4, California

Summary

Previous work under this contract had shown that alkynes coordinate with silver ion in aqueous solution, the solubility method being used to estimate the argentation constants. This work has now been extended by the isolation of several such coordination complexes in the crystalline state. Work has also been commenced on the measurement of argentation constants in aqueous solution by means of concentration cells.

Complexes of silver salts analogous to those with the alkynes have been prepared with several alkenes and with dioxane.

Several methods of synthesis of the hitherto unknown di-isopropylacetylene have been attempted, without success so far.

CONTENTS

PART 1.

The isolation of complexes of silver salts with alkynes.

Introduction.

As an accompaniment to a study of the coordination of silver salts with alkynes in aqueous solution, we are studying the reactions of silver salts with alkynes in the absence of a solvent medium with a view to obtaining these complexes in the pure state.

Coordination of the silver ion with the ethylenic double bond is well-known in aqueous solution, and several solid complexes of silver salts with alkenes have been prepared (see Part 4.). To prepare analogous complexes of silver ion with the acetylenic triple bond it is desirable to employ disubstituted acetylenes, to avoid complications due to the reactivity of acetylenic hydrogen atoms. No such complexes have hitherto been isolated. Taufen, Murray and Cleveland (J.A.C.S., 63, 3500 (1941)) reported di-amylacetylene, ethylbutylacetylene, and di-ethylacetylene to be insoluble in aqueous silver nitrate, and on this basis concluded that dialkylacetylenes did not coordinate with the silver ion. Dorsey (Thesis, C.I.T., 1950) has pointed out that the visual method employed by these workers is inadequate for the low solubilities found in these systems.

Experimental results.

1). System: 2-butyne - silver perchlorate.

Crystalline silver perchlorate reacts reversibly with 2-butyne at 25° to give a voluminous white powder of composition: $3(C_4H_6).AgClO_4$,

the reaction being complete within twenty four hours. This formula was established by microanalysis of the solid and by a vapor-pressure study of the system over a range of relative proportions of the reactants. The solubility of silver perchlorate in 2-butyne at 0° is less than 0.1% by weight, but this is sufficient for the solution to be able to plate with silver a copper wire immersed in it.

2). System: 2-pentyne - silver perchlorate.

Silver perchlorate is very soluble in 2-pentyne, and at some concentrations a system of two liquid phases is formed. At 25° the upper phase contains 10% silver perchlorate (by weight) and the lower phase 36%. Addition of more silver perchlorate to this two-phase system causes the lower layer to increase at the expense of the upper, and when the upper phase has disappeared the remaining liquid can dissolve even more than 36% silver perchlorate. Increase of temperature causes the upper phase to increase at the expense of the lower. When two liquid phases are present, the lower phase has m. p. -0.5° ± 0.2°; the upper phase freezes at a considerably lower temperature. These liquid phases were all more or less brown in color. The more dense of the two liquid phases was more brown than the other, but on freezing the former colorless crystals separated and the brown color entered the remaining liquid phase. The nature of the solid phase in equilibrium with a saturated solution of silver perchlorate in 2-pentyne was not investigated since it would be difficult to free it completely from the viscous solution. No lowering of the vapor pressure of 2-pentyne was detected when up to 13% of silver perchlorate

was dissolved in it. Raoult's law predicts a lowering of 3.2 mm. in such a solution, and the technique used would have detected a lowering of 0.3 mm. A copper wire immersed in these pentyne solutions became silver plated. The solutions containing 36% or more silver perchlorate exploded on contact with mercury, after a brief induction period.

3) System: 3-hexyne - silver perchlorate.

Silver perchlorate is very soluble in 3-hexyne to a syrupy brown solution, but systems of two liquid phases were not formed. The saturated solution contains about 32% silver perchlorate at 27°. On cooling this solution to -78° white needles are deposited, but they redissolve on warming to 0°. The concentrated solutions explode on contact with mercury and silver-plate copper, like the pentyne solutions.

4) System: 2-butyne - silver nitrate.

The solubility of silver nitrate in 2-butyne at 24° is about 1.5%. On cooling this solution to 0° crystals are deposited, but these have not yet been examined. On warming a mixture of silver nitrate with 2-butyne in a sealed tube to 65° a system of two liquid phases is formed: a colorless upper layer and a dark brown lower layer which rapidly deposits silver. On cooling, the lower liquid phase forms a mass of crystals at 44-45°.

5) System: 2-pentyne - silver nitrate.

On allowing powdered silver nitrate to stand at room temperature with excess 2-pentyne, this is slowly absorbed to form a mass of small

crystals, which occupy nearly three times the volume of the original silver nitrate. Reproducible analyses were not obtained for these crystals, but the approximate composition appeared to be $3(AgNO_3).2(C_5H_8)$. No crystals were obtained by warming silver nitrate with 2-pentyne and then cooling the solution. A small yield of crystals was, however, obtained when this procedure was repeated in the presence of acetone. These crystals had m. p. 147-148 d.

6) System: 3-hexyne - silver nitrate.

On allowing silver nitrate to stand with 3-hexyne at room temperature for eight weeks, the hexyne is absorbed with the formation of a crystalline complex. This was first observed by F. Carter. Analysis showed the complex to consist of $AgNO_3.C_6H_{10}$. G. Helmkamp found the solubility of silver nitrate in 3-hexyne at 25°, in the presence of water, to be very small. We have found that on heating silver nitrate with 3-hexyne to 80°, cooling to -78° and then re-warming to room temperature, a small yield of crystals is obtained. A better yield of this crystalline complex is obtained by recrystallizing silver nitrate from a mixture of 3-hexyne with acetone. On heating this complex in a melting-point tube, liquid was seen to appear with the solid at 46° and to disappear (presumably volatilize) at 76°. This is interpreted as the complex dissociating at 46° into its constituents, and this conclusion is supported by measurements of vapor pressures of the complex at different temperatures. Plots of log P against 1/t for the complex and for 3-hexyne gave straight lines intersecting at about 60° C., indicating that at this temperature the complex would have the same vapor pres-

sure as 3-hexyne, i.e., would dissociate. The value of 60° for this dissociation temperature is only approximate as the lines had to be extrapolated above room temperature (25°).

7) Systems with other alkynes.

Silver perchlorate dissolved in 2-heptyne and in 2-methyl-3-hexyne to brown, viscous liquids similar to the solutions in 3-hexyne. It dissolved in 2:2:5-trimethyl-3-hexyne to form two liquid phases, the lower one red in color. It did not appear to dissolve in, nor react with, di-tert.butyl acetylene. It did not dissolve in molten diphenylacetylene.

Silver nitrate yielded colorless crystals on standing with 2-methyl-3-hexyne, 2:2-dimethyl-3-hexyne, and 2:2:5-trimethyl-3-hexyne, similar in appearance to those obtained with 3-hexyne. No crystals were obtained from silver nitrate with 2-heptyne.

8) Systems with other silver salts.

Silver chloride, sulphate and acetate did not dissolve in, or react with, 2-butyne. Silver benzoate did not dissolve in molten diphenylacetylene.

Discussion of results.

The crystalline complexes of alkynes with silver nitrate that have been isolated resemble those of the alkenes in their general properties. They are colorless, mostly have definite melting points, and readily dissociate into their constituents.

The complex of silver perchlorate with 2-butyne is unusual in that the coordination number of the silver ion is three. This is interpreted as arising from the rigid, rod-like structure of the 2-butyne molecule which would favor hexagonal packing in the crystal and thus introduce a factor of three into the combining ratio.

A surprising feature is the great difference between the solubilities of silver perchlorate in 2-butyne ($< 0.1\%$) and in 2-pentyne ($> 36\%$). This may arise simply because 2-butyne, being a symmetrical, linear molecule, forms a non-polar solvent whereas 2-pentyne does not.

The question as to whether or not the concentrated solutions of silver perchlorate in 2-pentyne, 3-hexyne, 2-heptyne and trimethyl-3-hexyne are to be regarded as "liquid complexes" or as containing "complexes" is regarded as academic at this stage. Undoubtedly, strong interaction between the silver ions and the triple-bonds is responsible for the high solubilities encountered. The question as to whether or not true complexes exist in these solutions is, however, analogous to the classical problem of determining hydration numbers of ions in aqueous solution: in this field there have been nearly as many different results as there have been methods of investigation. The liquid complexes of silver nitrate with propylene and with 1-butene, described by A. W. Francis, appear to be different from the solutions obtained in the present work (with the possible exception of the warm solution of silver nitrate in 2-butyne) since they were insoluble in excess of the alkene and had definite dissociation temperatures.

PART 2

Argentation Constants of Alkynes by Means of Concentration Cells:

electrode development.

In order to obtain equilibrium constants which were undistorted by the presence of a carbon tetrachloride phase, as in the distribution method of S. Dorsey (Thisis, C.I.T.), and at alkyne concentrations which were not saturation, the method of concentration cells was studied. The utility of the method is strongly dependent upon the sensitivity and reproducibility of the electrodes used. Aside from these considerations the practical electrode for this purpose would be the simple silver-silver ion electrode. However, this electrode is rarely used since it is sensitive to the presence of oxygen and since reproducibility in electroplating is infrequent.

Preparation.

F. H. McDougall (J.P.C.C., 51, 1347 (1947)) described the preparation of a simple silver-silver ion electrode which was believed would be suitable for our purpose. This method, only slightly altered, produces out of seven electrodes made, four whose potentials are within thirty microvolts of one another. The present method consists of molding moist silver oxide around a platinum wire (.010 in.) helix 3 mm. in diameter and 8 mm. long. The platinum wire makes contact with mercury through the end of a pyrex tube. The moist silver oxide is decomposed to porous silver in a stream of nitrogen (H.P.D.. LINDE CO.) at a temperature of 430° ± 15°C. The electrodes are also cooled in a

stream of nitrogen. Electrodes when first prepared are lustrous white; however, when left unprotected for an hour, they become dull gray and develop potential differences.

Storage

Newly prepared electrodes can be stored without deterioration in a vessel evacuated by means of a mercury diffusion pump in conjunction with a two stage rotary pump.

Electrodes which have been used can be stored, after washing, in conductivity water at a reduced nitrogen pressure. Before actual use the electrodes are carefully dried with a filter paper, mercury is added, and all glass that would be exposed outside the cell is covered with loose fitting opaque tubing.

Restoration

Electrodes differing by a small potential, e.g., 190 microvolts, can sometimes be completely restored by an electrolytic purification; namely the one that F. H. McDougall used. A method that is more effective for greater potential differences uses hot concentrated nitric acid to dissolve the exposed gray silver. Solution of too much of the porous silver reduces the stability of the electrode; hence the latter method requires caution. The electrodes need careful washing after these processes to prevent contamination of the cell and storage vessel contents. Successful restoration of used electrodes by use of the furnace has not been achieved.

PART 3

Attempted Synthesis of 2,5-Dimethyl-3-hexyne (Diisopropylacetylene).

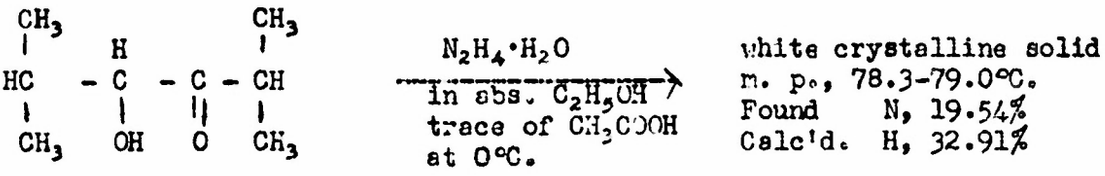
To complete the series of di-substituted 3-alkynes studied in regard to their coordination reactions, it was necessary to attempt the synthesis of 2,5-dimethyl-3-hexyne. Since the classic methods of alkyne synthesis, i.e., reaction of isopropyl halides with sodioalkynides and with acetylenic Grignard reagents, had failed due to dehydrohalogenation of the halide in the first case, and non-reactivity in the case of the Grignard synthesis, recourse to indirect methods was necessary.

The following procedures were adopted, and the work to this date was carried out along these lines except when it became apparent that the methods were valueless.

Synthetic Procedures

1. From isobutyroin through conversion to the dihydrazone, followed by destructive oxidation of this to the alkyne using yellow mercuric oxide; based on the general method of A. T. Blomquist, R. E. Burge Jr. and A. C. Suscay; (J. Am. Chem. Soc., 74, 3637 (1952)). Since isobutyroin was thought to be more reactive than sebacoin used by the above authors, the intermediate steps were modified using procedures that had been applied to compounds similar to isobutyroin.

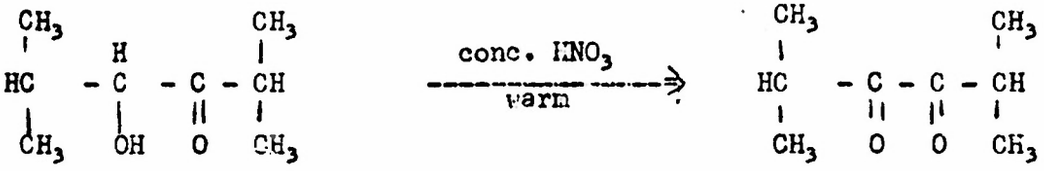
a. Conversion of isobutyroin directly to isobutyryl dihydrazone by a modification of the method of A. Basse and H. Klinger; (Ber. 31, 1218 (1898)). Hydrazine hydrate was used in place of phenylhydrazine, and sodium acetate was omitted.



white crystalline solid
m. p., 78.3-79.0°C.
Found N, 19.54%
Calc'd. H, 32.91%

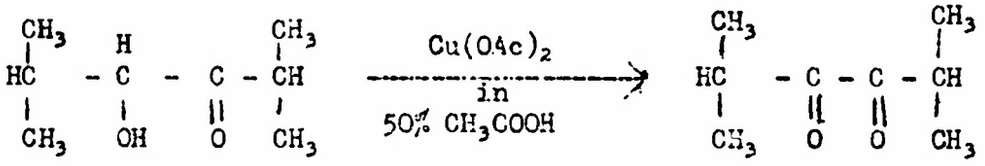
The method was abandoned due to incorrect nitrogen content.

b. Oxidation of isobutyroin to di-isobutyryl by the method of M. Fileti and G. Ponzio; (Journ. für prek. Chemie [2], 51, 502 (1895)).

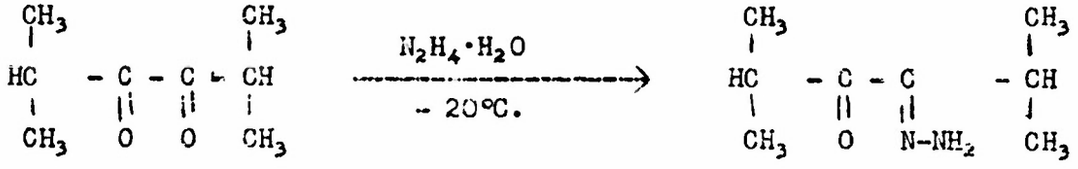


A very low yield was obtained.

c. Oxidation of isobutyroin to di-isobutyryl according to H. Block, et al. (Helv. Chim. Acta, 28, 741; 1410 (1945)): 36% yield obtained.

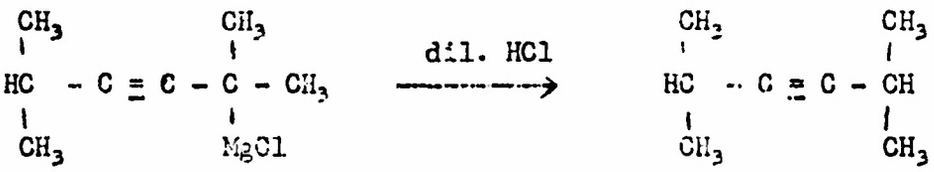


d. Formation of the monohydrazone of di-isobutyryl by the method due to O. Diels and K. Flaumer, (Ber., 49, 226 (1915)).



The liquid diketone was transformed almost completely to yellow-white crystals by this treatment; however, attempted recrystallization from 60-70° ligroin resulted in essentially complete hydrolysis of the white solid to the yellow diketone. This method was temporarily abandoned due to the above fact and a lack of starting materials. Further work on this method, under more careful conditions, may well prove of value in the final synthesis.

2. From 2-Chloro-2,5-dimethyl-3-hexyne, by reduction with magnesium:



This reaction was attempted on a semimicro scale using a sample of the crude starting materials prepared by G. K. Helmkamp. A solid addition product separated; and on hydrolysis of this a vigorous reaction, typical of Grignard reagents, took place.

To further investigate this reaction, the synthesis of 2-chloro-2,5-dimethyl-3-hexyne was attempted by the procedure due to G. F. Hennion and T. F. Banningan Jr., (J. Am. Chem. Soc., 68, 1202-4 (1946)), using 3-methyl-1-butyne as starting material. This failed, apparently due to the rearrangement of the 3-methyl-1-butyne to 3-methyl-1,2-butadiene dur-

ing storage in a sealed ampoule. It was felt that the complete synthesis of 3-methyl-1-butyne from isoamyl alcohol, in order to continue this line of attack, was not warranted.

3. From 2,5-Dichloro-2,5-dimethyl-3-hexyne, by reduction with magnesium, lithium aluminum hydride or butyl lithium. This procedure required the synthesis of 2,5-dimethyl-3-hexyne-2,5-diol, which was prepared after the method of G. Dupont (Ann. Chim. phys. [8], 30, 494-5 (1913)):

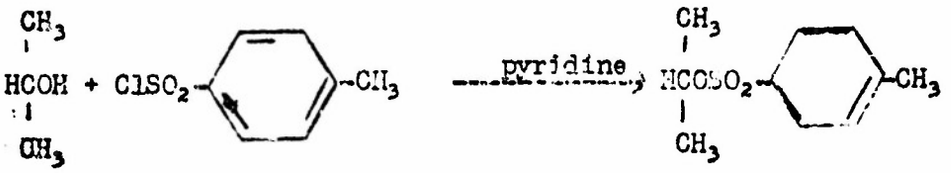
$$HC \equiv CH \xrightarrow{C_2H_5MgBr} BrMgC \equiv CMgBr$$

$$BrMgC \equiv CMgBr \xrightarrow{(CH_3)_2C=O} \xrightarrow{(dil.\ HCl)} H_3C - \underset{\displaystyle OH}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}} - C \equiv C - \underset{\displaystyle OH}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}} - CH_3$$

The above author also prepared the dichloro compound by treatment of the diol with hydrogen chloride at 0°C, but due to the question of isomerization to the corresponding 2,5-dimethyl-3,4-dichloro-2,4-hexadiene under these conditions, the present work is directed towards preparing the dichloroalkyne by treating the diol with thionyl chloride under appropriate conditions.

4. From BrMgC ≡ CMgBr, by reaction with isopropyl-p-toluene sulfonate. This procedure was based on the work of H. Gilman and N. J. Beaber, (J. Am. Chem. Soc., 45, 839-42 (1923)), who reacted various sulfonate esters with various Grignard reagents.

Isopropyl-p-toluensulfonate was prepared according to R. S. Tipson, M. A. Clapp and L. H. Cretcher, (Journ. Org. Chem., 12, 133-7 (1947)):



The final step in this synthesis has not yet been attempted.

PART 4

Complexes of cyclohexene, α-pinene, and nopinene, with silver perchlorate.

Introduction.

Many complexes of silver ion with unsaturated carbon compounds have been studied in aqueous solution by Lucas and his co-workers, and by Andrews and Keefer; but comparatively few such complexes have been isolated. The complex of silver perchlorate with benzene is well known and has been the subject of a recent X-ray crystallographic study (R. E. Rundle and J. H. Goring, J.A.C.S., 72, 5337 (1950)). S. Winstein and H. J. Lucas (J.A.C.S., 60, 836 (1938)) isolated solid complexes of silver nitrate and perchlorate with dicyclopentadiene; and recently Salomon (in "Cationic Polymerization and Related Complexes," edited by P. H. Plesch, Heffer, Cambridge, 1953, p. 62) has reported the melting points and compositions of crystalline complexes of silver nitrate with a number of conjugated dienes and with cyclohexene. The crystalline complexes of cyclooctatetraene, and its derivatives, with silver nitrate have been used for purifying these compounds (H. Reppe, O. Schlichtung, K. Klager and T. Toepel, Ann., 560, 1 (1948); A. C. Cope and F. A. Hochstein, J. Amer. Chem. Soc., 72, 2515 (1950)); and the cis and trans isomers of cyclooctene have been separated, utilizing their differences in solubility in aqueous silver nitrate (A. C. Cope, R. A. Pike, and C. F. Spencer, J. Amer. Chem. Soc., 75, 3212 (1953)). Salomon (loc. cit.) p. 62)) has referred to unpublished work on the purification of diprene via its complex with silver nitrate. A. W. Francis (J. Amer. Chem. Soc., 73, 3709 (1951))

treated propylene and 1-butene with silver nitrate, and obtained liquid complexes of variable composition and unusual properties.

The object of the present work was to obtain a crystalline alkene-silver salt complex that would be suitable for an X-ray crystallographic examination, with a view to determining the geometry of the silver-carbon bonds. This led, incidentally, to a new method of separating mixtures of α-pinene with nopinene and to the isolation, for the first time, of a crystalline derivative of nopinene from which nopinene may readily be regenerated.

Experimental results.

Cyclohexene reacts at room temperature with anhydrous silver perchlorate to produce a voluminous white powder of composition: $2(C_6H_{10})\cdot AgClO_4$. The same complex may be prepared in the form of large crystals by dissolving silver perchlorate in a warm mixture of equal volumes of acetone and cyclohexene, and slowly cooling to room temperature. Both α-pinene and nopinene react with silver perchlorate in a similar manner, yielding complexes of composition: $2(C_{10}H_{16})\cdot AgClO_4$; and crystalline complexes of the same composition may be prepared by recrystallizing silver perchlorate from the warm pinenes. These complexes have definite melting-points, and the pinenes may be recovered by treatment with water. The reaction with silver perchlorate affords a convenient method of separating mixtures of the two pinenes, since nopinene reacts in several minutes whereas α-pinene requires several hours for reaction. In one experiment, a mixture of equal masses of the two pinenes was treated with sufficient silver perchlorate to combine with only one, the mixture

allowed to stand for two days, and the liquid phase then separated from the solid by high-vacuum distillation (pinenes volatilize from their silver perchlorate complexes very slowly under these conditions). The pinene mixture obtained from the liquid phase (47%) consisted of 85% α-pinene and 15% nopinene; that from the solid phase, after water-treatment (39%), consisted of 89% nopinene and 11% α-pinene.

Discussion of results.

The crystalline complex of cyclohexene with silver perchlorate is of a similar composition to that with silver nitrate reported by Salomon (loc. cit.) but is more convenient for X-ray examination since it melts at 136°, whereas the silver nitrate complex melts at room temperature.

The crystalline complexes of the pinenes with silver perchlorate are of importance owing to the paucity of crystalline derivatives formed by such compounds. The only reported crystalline derivatives of nopinene are the oxidation product nopinic acid, and the addition compound with carbon tetrachloride (G. Dupont, G. Clément and R. Dulon, Bull. soc. chim. France, 1950, 1056): from neither of these is nopinene readily recoverable. Several methods of separating mixtures of α-pinene with nopinene are known but the method described above promises to be the simplest, on the laboratory scale at least. Fractional distillation gives high yields of the separated products (D. M. Oldroyd and L. A. Goldblatt, Ind. Eng. Chem. Anal., 18, 761 (1946)) but requires a highly efficient column with very slow take-off: Oldroyd and Goldblatt (loc. cit.) operated a Podbielniak column for one week in order to separate 500 g. of a mixture of equal

parts of α-pinene and nopinene into fractions of 99.5% purity with only a 52 g. intermediate fraction. G. Austerweil (Chem. Ztg., 50, 5 (1926)) has described a method for this separation utilizing the different solubilities of the two pinenes in aqueous ethanol, but this method is useful only for large-scale work and has probably been superceded industrially by high-efficiency fractionation.

Experimental Details

Materials. - Silver perchlorate (anhydrous) was used as purchased from G. F. Smith and Co.; cyclohexene had been prepared by Dr. N. Koenig, and had $(n)_D^{25}$ 1.4441. The pinenes were samples of better than 99.9% purity, especially prepared by the Glidden Chemical Co., and were stored before use under vacuum in sealed ampoules: α-pinene had $(n)_D^{25}$ 1.4631, $(\alpha)_D^{25}$ 25.6° in dm. tube; nopinene had $(n)_D^{25}$ 1.4765, $(\alpha)_D^{25}$ -18.2° in dm. tube.

Analyses. - Silver determinations on the cyclohexene complexes and on the amorphous α-pinene complex were by conventional thiocyanate titration in the presence of the hydrocarbon: other analyses were by Dr. A. Elek.

Preparation of cyclohexene-silver perchlorate complex. - Excess cyclohexene (12 ml.) was added to crystalline silver perchlorate (2.63 g.): a rapid exothermic reaction occurred and the perchlorate was converted to a voluminous white powder which was then filtered off; yield, 4.28 g.

Anal. - C, 38.91; H, 5.53; Ag, 28.97, 28.93; Cl, 9.77%.

$2(C_6H_{10})\cdot AgClO_4$ requires: C, 38.79; H, 5.42; Ag, 29.04; Cl, 9.56%.

Crystallisation of cyclohexene-silver perchlorate complex. - Silver perchlorate (4.05 g.) was dissolved in a warm mixture of cyclohexene (5 ml.) with acetone (5 ml.), and the solution cooled in ice. The complex crystallized out in the form of rectangular plates, which were filtered off; yield, 5.02 g.

Anal. - C, 37.97; H, 5.41; Ag, 29.00, 28.93; Cl, 9.66%.

Recovery of cyclohexene from silver perchlorate complex. - The powdered complex (3.64 g.) was treated with water (15 ml.) and shaken until all the solid had dissolved. The upper liquid layer thus formed (1.6 ml.) was dried overnight with sodium and then distilled under vacuum; yield, 1.21 g. of liquid having $(n)^{25}_{D}$ 1.4438. This represents a 75% recovery of cyclohexane. The lower aqueous layer yielded only a trace of a second liquid phase when treated with excess ammonium hydroxide.

Preparation of α-pinene complex. - Silver perchlorate was left to stand with α-pinene at room temperature for several hours. The solid swelled considerably; filtration yielded a white powder.

Anal. - Ag, 22.4, 22.6%. $2(C_{10}H_{16})\cdot AgClO_4$ requires 22.6% Ag.

For the preparation of the crystalline complex, silver perchlorate (ca. 0.2 g.) was left with α-pinene (10 ml.) at room temperature for three hours and the mixture then warmed to dissolve the complex. Cooling to room temperature yielded 0.1 g. of small crystals; m. p. 75-76°: on further heating, the molten complex blackened suddenly at 125°. On heating in a test-tube the complex exploded mildly.

Anal. - C, 50.36; H, 6.72; Ag, 22.64; Cl, 7.26 %

$2(C_{10}H_{16})\cdot AgClO_4$ requires: C, 50.03; H, 6.67; Ag, 22.50; Cl, 7.39%.

Preparation of nopinene complex. Silver perchlorate reacted rapidly with nopinene at room temperature, the mixture becoming warm and much white powder being produced. The crystalline complex was prepared by leaving silver perchlorate (ca. 0.4 g.) to stand with nopinene (10 ml.) for five minutes, heating to dissolve the complex so formed, and cooling to room temperature: Yield, 0.4 g. crystals, m.p. 108-109°. Like the complex with α-pinene, the molten complex blackened suddenly at about 125°, and exploded mildly on heating in a test-tube.
Anal. C, 49.00; H, 6.56; Ag, 22.40; Cl, 7.21%.

The separation of nopinene from α-pinene. Compositions of pinene mixtures were determined by measurements of optical rotations and refractive indices. The optical rotation method was first used by Darmois (These, Paris, 1910); and refined by R. E. Fuguitt, W. D. Stallcup and J. E. Hawkins (J. Amer. Chem. Soc., 64, 2978 (1942)), who found only small deviations from Biot's law. A calibration curve was constructed for the refractive indices of mixtures of the two pinenes, the deviation from linearity showing a maximum at equimolar concentrations, corresponding with a concentration difference of 2%; the equation given by Fuguitt et al. (loc. cit) predicts a deviation of 4%.

The starting mixture contained 49.7% α-pinene and 50.3% nopinene by weight: it had $(n)^{25}_{D}$ 1.4695; $(\alpha)^{25}_{D}$ +3.8°. Silver perchlorate (16.02 g.) was treated with 41.89 g. of this mixture, and left to stand at 20° for 43 hours. The liquid phase was removed from the mixture by short-path, high-vacuum distillation into a tube cooled by liquid air, the reaction vessel being maintained at room temperature. This method of separating the phases was found to give better results

than filtration, owing to the difficulty of completely removing traces of liquid from the solid phase by suction.

The distillate contained traces of water, probably present originally in the silver perchlorate. It was dried over potassium carbonate and redistilled in the same apparatus, yielding 19.7 g. of clear liquid having: $(n)^{25}_{D}$ 1.4652; $(\alpha)^{25}_{D}$ +19.2°. These constants correspond with those of a mixture containing 85% α-pinene and 15% nopinene.

The solid phase was shaken with water (20 ml.) until all the solid had dissolved, and the upper layer (21.5 ml.) separated. It was dried over potassium carbonate and distilled in the vacuum apparatus: yield, 16.3 g. of clear liquid having $(n)^{25}_{D}$ 1.4749; $(\alpha)^{25}_{D}$ -13.8°. These constants correspond with those of a mixture containing 89% nopinene and 11% α-pinene.

PART 5

The System: Silver Perchlorate - Dioxane

Few complexes in which the silver ion is coordinated with an oxygen atom have been isolated (N. V. Sidgwick, "The Chemical elements and their Compounds," O.U.P., Oxford, 1950, 141). J. A. Skarulis and J. E. Ricci (J. Am. Chem. Soc., 63, 3429 (1941)) obtained evidence for the formation of a solid complex between silver nitrate and dioxane, to which the formula $8(AgNO_3).C_4H_8O_2$ was tentatively assigned on the basis of silver determinations. G. Salomon (Rec. trav. chim., 68, 905 (1949)) observed that silver perchlorate was insoluble in dioxane and deduced from this that no complex was formed. In the complexes of silver nitrate with pyrone (R. Willstätter and R. Pummerer, Ber. deut. chem. Ges., 37, 3747, (1904)), with phenol (C. R. Bailey, J. Chem. Soc., 1930, 1534), and with cyclooctatetraenyl phenyl ketone (A. C. Cope and D. J. Marshall, J. Am. Chem. Soc., 75, 3208 (1953)) it is not known whether the silver ions are attached to the oxygen atoms or to other parts of the molecules, since similar compounds not containing oxygen also form silver complexes.

We have found that although silver perchlorate is insoluble in dioxane it reacts slowly with dioxane to produce a voluminous white powder of composition $3(C_4H_8O_2).AgClO_4$, which occupies about six times the volume of the original silver perchlorate. The reaction between the well-dried reactants at 25° is very slow: it is accelerated by traces of water (with 0.5% water, re-

action complete within five days) and by heat. The conversion of silver perchlorate, in the presence of excess moist dioxane, to this complex is quantitative (99%); and dioxane may quantitatively (97%) be removed from the complex by high-vacuum distillation. The same complex may be produced in the form of large crystals by dissolving silver perchlorate in a warm mixture of equal volumes of dioxane and acetone, and cooling to room temperature. On heating the crystalline complex it does not melt, but slowly evolves dioxane and is converted to a powdery solid at about 120°. Further heating causes this solid to shrink and finally to melt to a bubbling brown liquid above 400°. On heating in a flame, the complex burns quietly with occasional bright spurting; it does not appear to be explosive.

This work, together with our work on unsaturated hydrocarbons emphasizes the fact that the insolubility of a metal salt in an organic liquid is no evidence that the salt and the liquid will not form a complex under slightly different conditions.

Experimental Details

Dioxane and anhydrous silver perchlorate were both of "reagent" grade. Silver analyses were by conventional thiocyanate titration; carbon, hydrogen and chlorine analyses were by Dr. A. Elek.

Preparation of powdered complex. - Silver perchlorate (1.81 g.), dioxane (10 ml.) and water (0.05 ml.) were shaken together at 25° for 5 days. Filtration yielded 4.42 g. of white powder. Adhering dioxane was removed by pumping to 5 mm. mercury for 1 min. The

product weighed 4.10 g., and evacuation for another minute resulted in the further loss of only 0.01 g.

Anal. - Ag, 23.0, 23.1; C, 30.1; H, 5.14; Cl, 8.57 %. $3(C_4H_8O)_2 \cdot AgClO_4$ requires: Ag, 22.9; C, 30.6; H, 5.10; Cl, 7.52%.

Preparation of crystalline complex. - Silver perchlorate (2.2 g.), dioxane (15 ml.) and acetone (15 ml.) were warmed until the solid had dissolved, and then cooled to room temperature. The resulting crystals were filtered off, washed with dioxane, and freed from excess dioxane by a current of dry air: yield 3.4 g.

Anal. - Ag, 23.0; 23.1; C, 29.9; H, 5.13; Cl, 7.60%.

Recovery of dioxane from complex. - A wide, inverted U-tube, connected to a high-vacuum line via a stopcock, connected the flask containing the crystalline complex (3.35 g.) with the receiver. High-vacuum distillation from the flask at 70° to the receiver cooled in liquid nitrogen yielded, after 3 hours, 1.85 g. of colorless liquid. A negligible amount collected after a further 45 mins. The distillate was treated with sodium until the slight effervescence had ceased, and re-distilled in the same apparatus. The distillate had $(n)_D^{25}$ 1.4198; m. p. 11.3°: dioxane has $(n)_D^{25}$ 1.4201 (C. H. Schneider and C. C. Lynch, J. Am. Chem. Soc., 65, 1063 (1943)), and m.p. 11.6° (J. Gillis and A. Delaunois, Rec. trav. chim., 53, 186 (1934)).

Solubility of silver perchlorate in dioxane. - Silver perchlorate (ca. 1 g.), contained in a glass tube integral with a vacuum system, was dried by evacuation to 10^{-3} min. mercury pressure for

18 hours. Dioxane (10 ml.), dried over sodium, was distilled through the vacuum system directly on to the silver perchlorate, and the tube then sealed and removed from the system. The tube and contents were left to stand at room temperature (25° ± 5°), with occasional shaking, for 20 days. The tube was then opened and 5 ml. of the supernatant liquid removed. This was evaporated to dryness under vacuum, the residue dissolved in water (2 ml.) and hydrochloric acid (2 ml. of 0.1 N) added: the solution remained quite clear.

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